

In Situ X-ray Diffraction Studies of the Formation of AlF_3 Catalysts and Their Structural Correlation to Pure Phases

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Introduction: The increased demand to develop environmentally friendly alternatives to chlorofluorocarbons (CFCs) has resulted in the discovery of new catalyzed halogen exchange, elimination, and isomerization reactions.^[1] Alumina is widely used as a support or catalyst in these reactions. The reactions that occur over alumina containing catalysts often require periods of activation, where critical structural changes occur to both the surface and bulk of the catalyst, the result being O/F or O/Cl exchange.^[2] There is some discrepancy in the literature as to which AlF_3 phase is formed during these activation procedures, which typically involve fluorination of the alumina with a reagents such as HF or hydrofluorocarbons.^[3]

Methods and Materials: To further understand the structural changes that occur to these catalysts a “flow cell” for studying catalysis *in situ* has been developed, which allows for accurate temperature control, time-resolved data collection, and quantitative in-line analysis of reaction products. In these experiments the fluorination of $\gamma\text{-Al}_2\text{O}_3$ was studied using HCFC-22 (chlorodifluoromethane) as the fluorinating agent. Time resolved powder patterns were collected in the temperature range from 300 – 500 °C (**Figure 1a**). The rhombohedral to cubic phase transition of $\alpha\text{-AlF}_3$ was also examined in the same temperature regime for comparison with the fluorinated material.

Results: By utilizing solid state NMR data in conjunction with the *in situ* diffraction data we were able to identify the fluorinated $\gamma\text{-Al}_2\text{O}_3$ material as being structurally similar to rhombohedral $\alpha\text{-AlF}_3$. The fluorinated catalyst and $\alpha\text{-AlF}_3$ are both rhombohedral and are based on a distorted ReO_3 structure, but the fluorinated $\gamma\text{-Al}_2\text{O}_3$ possesses a larger Al-F-Al bond angle, which does not vary as much in the temperature regime from 300 – 500 °C as does that of $\alpha\text{-AlF}_3$ (**Figure 1b**). In addition, no evidence for the phase transition that occurs at approximately 460 °C in $\alpha\text{-AlF}_3$, and which involves an abrupt increase in Al-F-Al bond angle, was observed for the catalyst.

Conclusions: We have shown that structural changes do exist between fluorinated alumina (an active catalyst for the disproportionation of CFCs and HCFCs) and $\alpha\text{-AlF}_3$ (an inactive catalyst for the same). This work has provided a foundation for understanding why different preparatory methods yield materials with drastically different catalytic activities.

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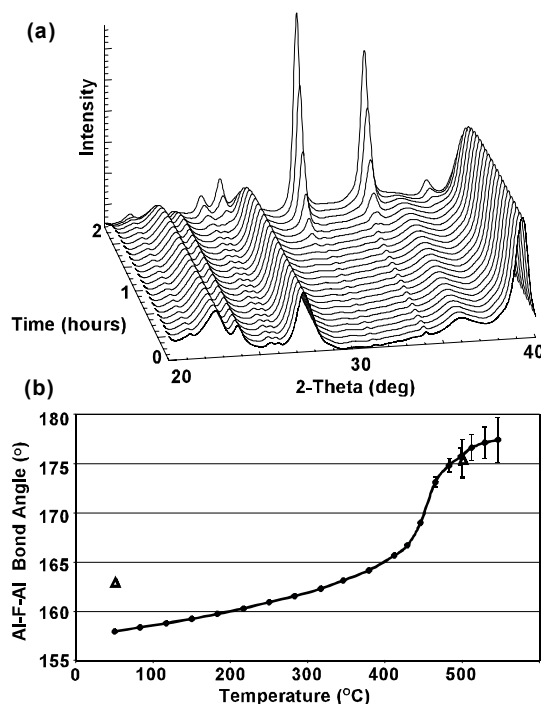


Figure 1. (a) *In situ* diffraction experiment showing the formation of AlF_3 from $\gamma\text{-Al}_2\text{O}_3$ and HCFC-22. The figure shows a portion of the temperature ramp to 425 °C, (one hour at 300 °C, one hour ramp to 425 °C). (b) Graph of Al-F-Al bond angle vs. temperature for a pure sample of $\alpha\text{-AlF}_3$ (circles) and the fluorinated catalyst (triangles).